Trap-Assisted Recombination in Disordered Organic Semiconductors

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Published in:
Physical Review Letters

DOI:
10.1103/PhysRevLett.107.256805

Publication date:
2011

Supporting Information

Trap-assisted recombination in disordered organic semiconductors

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SECTION 1; Parameters for the modeling.

Hole transport:

The hole mobility of MEH-PPV is dependent on the charge carrier density *p*, the applied electric field *E*, and temperature *T*. The density dependence of the mobility dominates the SCL *J–V* characteristics at room temperature, whereas the field-dependence becomes more important at low temperature. From a numerical solution of the master equation for hopping transport in a disordered energy system with a Gaussian density of states, a charge-transport model has been developed by Pasveer *et al*. (Phys. Rev. Lett. **94**, 206601 (2005)) that takes both effects into account. It has been demonstrated that the mobility can be described as:

$$\mu_p(T,p,E) \approx \mu_p(T,p) f(T,E) \ , \tag{S1}$$

with $\mu_p(T,p) = \mu_0(T)\exp[\frac{1}{2}\hat{\sigma}^2 - \hat{\sigma})(2pa^3)^{\delta}]$, (S2)

$$\mu_0(T) = \mu_0 c_1 \exp(-c_2\hat{\sigma}^2) \ , \tag{S3}$$

$$\delta = 2\frac{In(\hat{\sigma}^2 - \hat{\sigma}) - In(In4)}{\hat{\sigma}^2} \ , \tag{S4}$$

$$\mu_0 = \frac{a^2 \upsilon_0 e}{\sigma} \ , \tag{S5}$$

and $f(T,E) = \exp\{0.44(\hat{\sigma}^{3/2} - 2.2)[\sqrt{1+0.8(\frac{Eea}{\sigma})^2} - 1]\}$ (S6)

where $\hat{\sigma} \equiv \sigma / K_b T$ and σ the width of the Gaussian, a is the lattice constant.

Modeling of the hole transport of the 140nm MEH-PPV device comprising of the sandwich structure ITO/PEDOT:PSS/MEH-PPV/Au yields a μ_0 of 6.4×10^3 m^2 V^{-1} s^{-1}, σ of 0.143 eV and a of 1.5×10^{-9} m. In Fig. S1 the *J–V* characteristics are represented, together with the numerically calculated characteristics using the field- and density dependent mobility. The field- and density dependent mobility is included in the calculation of the space-charge limited current by solving the coupled equations

$$J = p(x) e \mu(T, p(x), E(x)) E(x) \ ,$$

$$\frac{dE}{dx} = \frac{e}{\varepsilon_0 \varepsilon_r} p(x) \ ,$$

and $V = \int_0^L E(x)dx$ (S7)

where x is the distance from the injecting electrode, and L is polymer thickness.

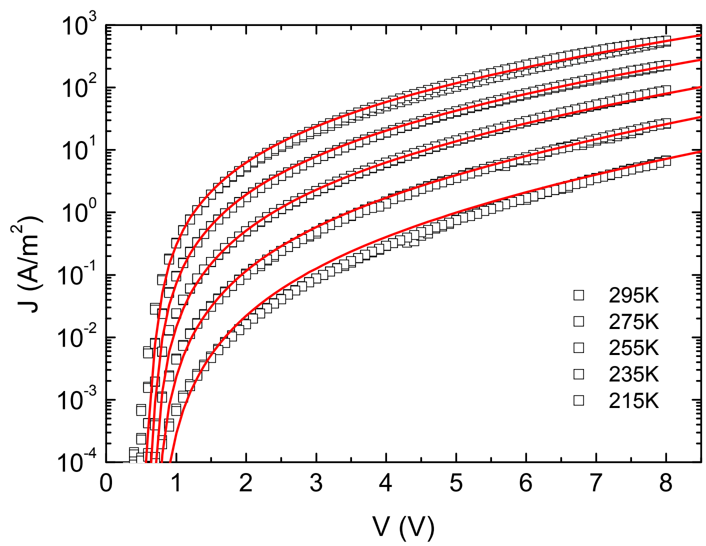

Figure S1. MEH-PPV 140 nm holy only device and the corresponding fits.

Electron transport:

For MEH-PPV it has been proven by n-type doping experiments that the free electron and hole mobilities are equal, $\mu_p = \mu_n$ and that the current is limited by traps. For this study an exponential trap distribution is used which we solve numerically, but it closely follows the Mark and Helfrich formalism, as described by Mandoc *et al.* (Phys. Rev. B 75, 193202 (**2007**)) and Nicolai *et al.* (Phys. Rev. B 83, 195204 (**2011**)). In this numerical calculation, a relation between free and trapped carriers is used, given by

$$n_t = N_t \left(\frac{n}{N_c} \right)^{T/T_t}, \qquad \text{(S8)}$$

with T_t representing the trap temperature of the exponential trap distribution, N_t the amount of traps, and N_c is the number of states in the Gaussian DOS, T the temperature. As explained by Mandoc *et al.* (Phys. Rev. B 75, 193202 (**2007**)), for a trap distribution that is separated by an energy E_{tc} from the LUMO, an effective density of traps has to be used, given by:

$$N_t e^{(E_{tc}-E_a)/kT_t} \qquad \text{(S9)}$$

with E_a a characteristic energy given by $\sigma^2/2kT$, σ the width of the Gaussian DOS, N_c the number of states in the Gaussian DOS and T the temperature. In Figure S2, a fit of an MEH-PPV electron-only device is shown, using for μ_n the same values as reported above for the hole mobility μ_p (E,p,T). For the trap distribution we find a T_t of 1500 K, and we used σ= 0.105 eV.

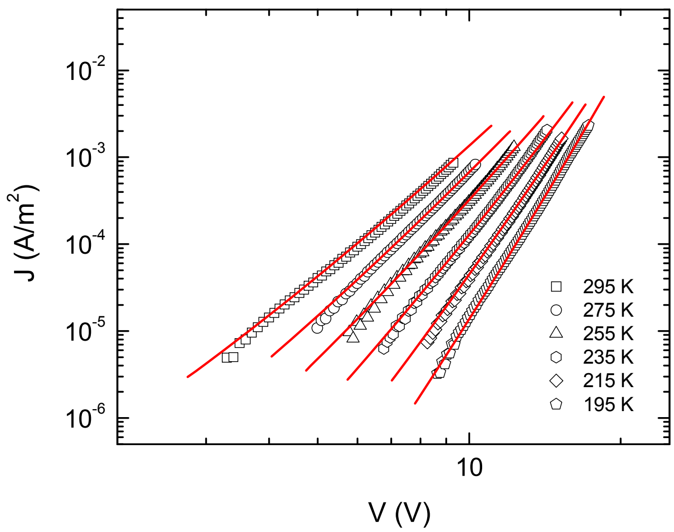

Figure S2. MEH-PPV 270 nm electron-only device and the fits.

Solar cell:

For the solar cell modeling of the 138 nm MEH-PPV device, the hole transport and electron transport parameters are combined. The general description for the device model for the solar cell is found in Koster *et al.* (Phys. Rev. B 72, 085205 (**2005**)). The bimolecular recombination is of the Langevin type:

$$B_L = \frac{q}{\varepsilon}(\mu_n + \mu_p)\,. \tag{S10}$$

In the absence of traps, where Langevin recombination is the dominant recombination process, the response of V_{OC} on light intensity is given by:

$$V_{OC} = \frac{E_{gap}}{q} - \frac{kT}{q}\ln\left(\frac{(1-P)B_L N_{CV}^2}{PG}\right) \tag{S11}$$

In this equation the V_{OC} is related to the light intensity which is directly proportional to the generation rate G. When considering trap-assisted recombination, the Shockley Read Hall (SRH) relation is used:

$$B_{SRH} = C_n C_p N_t / \left[C_n(n+n_1) + C_p(p+p_1)\right], \tag{S12}$$

where C_p and C_n denote the capture coefficients and are fitted as constants. For the simulation of both recombination processes, the SRH recombination is added to the Langevin in the model.

The parameters for the calculation of the dissociation probability P in the Onsager-Braun model (Onsager, Phys Rev. 54, 554 (**1938**) and Braun, J. Chem. Phys. 80, 4157 (**1984**)) are:

G_{max} (m^{-3})	e/h Pair distance, a (nm)	Decay rate, k_f (s^{-1})
5.5×10^{27}	0.6	3.5×10^{-6}

The generation rate is considered to be field dependent following $G(T,E) = G_{max}P(T, E)$ (Mihailetchi *et al.* Phys. Rev. Let. 93, 21 (**2004**)).

For more details see: Lambert Jan Anton Koster - "Device physics of donor/acceptor-blend solar cells" - MSC PhD thesis series 2007-4, ISBN-13: 9789036729413 and Valentin Dan Mihailetchi – "Device Physics of Organic Bulk Heterojunction Solar Cells"- MSC PhD thesis series 2005-14, ISSN: 1570-1530.

SECTION 2; Red and blue emission from a white copolymer.

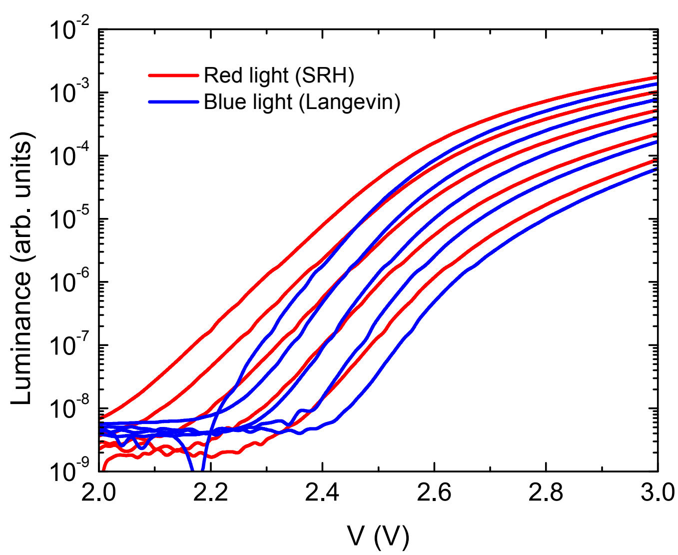

*Figure S3. The temperature dependence of the red (550 nm longpass filter) and the blue light (blue dichroic filter) of a white-light-emitting copolymer (*De Kok *et al.* Thin Solid Films 518, 5265 (2010) and Parshin *et al.* J. Appl. Phys. 103, 113711 (2008)).